

Ultrasonic Studies of Tetraethylammonium Bromide and Tetrapropylammonium Bromide in DMF-Water Systems at 303 K, 308 K and 313 K

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ABSTRACT

Ultrasonic velocities in solutions of tetraethylammonium bromide (TEAB) and tetrapropylammonium bromide (TPAB) in 10, 20 and 30 %w/w N,N-dimethylformamide (DMF)-water mixtures were measured at 303 K, 308 K and 313 K by using pulse echo overlap method at a frequency of 3 MHz. The ultrasonic velocity, density, and viscosity were used to calculate the adiabatic compressibility, apparent molal compressibility, apparent molal volume, limiting apparent molal compressibility, and limiting apparent molal volume. The observed variation in these parameters with respect to the molality highlights the type of interaction in the electrolytes and the structure making property of the salts.

Keywords Adiabatic compressibility, apparent molal compressibility, apparent molal volume, ion-ion and ion-solvent interaction.

1. INTRODUCTION

Ultrasonic studies have gained importance in recent years in the fields of medicine, engineering, agriculture and industry. In chemistry, such studies are used to investigate various chemical processes that play a major role in synthetic work¹.

Recently, ion-ion interactions and ion-solvent interactions for the tetraalkylammonium salts have been reported from density and viscosity measurements. Tetraalkylammonium salts afford an important class of organic compounds, which are used as phase transfer catalysts (PTC) However, their solution behavior is in

particular attractive for study because they include both hydrophobic and hydrophilic groups. We have attempted here to derive information on this regard from the experimental measurements of ultrasonic velocities and densities of TEAB and TPAB in binary mixtures of DMF-water.

2. EXPERIMENTAL DETAILS

The chemicals used for this study were of AR grade. DMF (Sigma-Aldrich) and TEAB and TPAB (Fluka) with purities better than 99 % were used as such. The ultrasonic velocity of the electrolytic mixtures was measured using the pulse echo overlapping method at a fixed frequency of 3 MHz with an uncertainty of 0.1 %. A more detailed description of the equipment may be found elsewhere¹⁵. The measuring cell temperature was maintained by using an electronically controlled thermostat having an uncertainty of ± 0.01 K. The density of the mixtures was measured using a specific gravity bottle with an uncertainty of ± 0.1 kg.m⁻³. The viscosity measurements have been carried out using an Ostwald viscometer. The overall uncertainty of the measurement of viscosity is ± 0.001 N.s.m⁻².

3. RESULTS AND DISCUSSION

The experimental values of density, viscosity, and velocity as a function of the concentration of TEAB/TPAB salt in different DMF aqueous solutions at 303 K, 308 K and 313 K have been reported in Table 1. The calculated values of the adiabatic compressibility, apparent molal compressibility, and apparent molal volume are reported in Table 2. The values of the limiting apparent molal compressibility,

limiting apparent molal volume, and the constants S_k and S_v for TEAB and TPAB salts are presented in Table 3. The plots of molality versus ultrasonic velocity at a single temperature 303 K for the two salts in 10, 20, and 30 %w/w DMF-water mixture are shown in Figure 1 and 2. The variation of adiabatic compressibility, apparent molal compressibility and apparent molal volume with concentration of salts in these mixtures studied.

From Table 1, ultrasonic speeds in the electrolytic solutions (TEAB/TPAB) were found to vary linearly with increasing molalities of the solutions as well as with increasing the concentration of DMF in solvent composition. The molality of electrolytic solutions increases due to formation of free ions in the solution which leads to increase in ultrasonic speeds. Moreover, the ultrasonic speeds are increases due to decrease in water solvation effect on electrolytes with increase in DMF concentration. This might be due to the electrostatic effect of a solvent on an electrolyte. The variation of the sound speed of electrolytic solutions with molality in water can also be expressed in terms of derivatives of density (ρ) and adiabatic compressibility (β):

$$\frac{dU}{dm} = -(U/2) \left[\left(\frac{1}{\rho} \right) \left(\frac{d\rho}{dm} \right) + \left(\frac{1}{\beta} \right) \left(\frac{d\beta}{dm} \right) \right] \quad (6)$$

The above equation shows that the molality dependence of the ultrasonic velocity is determined by the behavior of the density (ρ) and adiabatic compressibility (β) as the concentration is varied. The quantity $(d\rho/dm)$ is positive, while $(d\beta/dm)$ is negative in the present case. Since the values of $(1/\beta) d\beta/dm$ are larger than those of $(1/\rho)$

dp/dm for the salt, the molality derivative of the sound velocity (dU/dm) is positive which agrees with previous results²⁰, for potassium thiocyanate, sodium perchlorate, magnesium chloride, and beryllium perchlorate in DMF electrolytic solutions. In these salt solutions, the ions of opposite charges are dissociated due to interactions between the ions and solvent, and there will be a cloud of ions of positive and negative charges around a solvated finite charge ion in solution. The Br^- ions associate themselves with water molecules and also with a complex of DMF-water mixture²², resulting in an increase in the ultrasonic velocity and hence a decrease in the compressibility. Therefore, solvent molecules around the solute ions increase as a consequence of ion-solvent interactions suggesting an increase of intermolecular forces and may affect the structural arrangement.

The adiabatic compressibility (β) decreases and the density (ρ) increases with increasing concentration of the solutions. It is related to the ultrasonic velocity, (U) and density, (ρ) data of electrolytic solutions. Since β and U are known to be inversely proportional to each other, these variations have been found to be linearly convergent in the case of electrolytic solutions that show weak interactions. This decrease in the adiabatic compressibility is expected due to the structure-making effect of TEAB and TPAB.

From Table 2, ϕ_k values are negative for the electrolytic solutions over the entire range of molality and temperature. The ϕ_k values decrease with an increase in DMF content and with an increase in temperature. For the electrolytic solutions, the maximum negative value of ϕ_k occurs at a concentration

of 10 % of DMF. All the above observations clearly suggest that the ϕ_k values for the electrolytic solution are comparatively higher than that of the solvent, thereby indicating a strong ion-solvent interaction. Since a larger number of water molecules are available at a lower DMF concentration (10 %) the chances for dissolution of the solute in solvent are highly favored. This is indicated by the maximum ϕ_k values at 10 % DMF concentration for the systems. The limiting apparent molal compressibilities ϕ_k^o and S_k for each of the electrolytic solutions have been computed by a least-squares method. From Table 3, it is found that ϕ_k^o values are negative for TEAB and TPAB in DMF-water solutions and decrease on lowering the concentration of water. The negative ϕ_k^o values may be due to a loss of compressibility of the solvent due to strong electrostrictive forces of ions. The corresponding S_k values which indicate the solute-solvent interactions²⁵ decrease with an increase in temperature.

The apparent molal volume behaves in a similar fashion as that of apparent molal compressibility in the salt solution. The negative values of ϕ_v indicate electrostrictive solvation of ions. To examine the solute-solvent interactions, ϕ_v^o values are negative and increase with a rise in temperature and decrease with an increase in the amount of DMF in the mixtures. This indicates the presence of solute-solvent interactions, and these interactions are strengthened with a rise in temperature and weakened with an increase in the amount of DMF in the mixed solvent. More and more solute is accommodated in the void space left in the packing of large associated solvent

molecules with the addition of DMF to the mixture. Similar explanations have also been suggested for ammonium aluminum sulphate and potassium aluminum sulphate in DMSO-water by Parmar²⁷ and NaI, KI in DMF-propanol.

Table. 1 Density (ρ) and velocity (U)

Molality of salt (m)	ρ (kg. m ⁻³)	U (m.s ⁻¹)				
	303	308	313	303	308	313
TEAB						
DMF- Water (10:90 %w/w)						
0.0000	977.6	975.4	968.2	1564.2	1569.3	1572.9
0.2001	981.1	979.4	976.1	1577.5	1579.3	1580.1
0.4013	983.2	980.9	979.2	1582.1	1584.2	1586.6
0.6002	984.7	984.2	982.3	1588.3	1589.5	1592.7
0.8016	986.6	985.3	984.1	1592.6	1595.8	1596.0
1.0001	990.9	988.7	986.5	1598.6	1599.7	1602.2
DMF- Water (20:80 %w/w)						
0.0000	975.4	972.5	965.3	1607.7	1610.1	1612.4
0.2009	979.6	974.1	971.2	1608.5	1612.1	1615.7
0.4001	981.1	977.8	975.4	1615.8	1616.8	1617.0
0.6000	984.0	982.0	977.3	1620.2	1624.6	1626.3
0.8002	984.5	983.6	978.1	1626.5	1630.8	1632.9
1.0010	986.2	985.7	982.7	1635.4	1638.3	1639.2
DMF- Water (30:70 %w/w)						
0.0000	970.6	969.1	963.8	1622.4	1635.9	1638.6
0.2002	974.9	973.3	970.1	1640.6	1641.1	1647.3
0.4003	976.7	975.8	974.2	1643.2	1647.5	1653.4
0.5999	981.2	980.0	976.3	1649.8	1650.4	1657.4
0.8002	983.7	982.3	979.8	1659.5	1661.9	1666.5
1.0002	985.5	984.5	981.2	1662.3	1666.3	1673.4
TPAB						
DMF- Water (10:90 %w/w)						
0.2002	985.9	981.8	979.6	1582.2	1584.1	1588.2
0.4001	987.3	985.3	982.4	1587.5	1590.6	1594.6
0.6003	990.2	987.1	985.3	1593.8	1595.7	1599.8
0.8002	993.1	992.2	988.5	1598.7	1603.9	1610.1
1.0003	995.5	994.3	991.2	1605.6	1611.3	1617.3
DMF- Water (20:80 %w/w)						
0.2003	983.2	979.1	975.2	1610.5	1615.7	1620.9
0.4006	984.9	982.3	976.6	1618.8	1623.4	1627.7
0.6003	986.3	984.7	978.1	1624.3	1629.5	1633.5
0.8000	989.4	987.8	980.4	1635.1	1637.6	1642.1
1.0004	992.5	989.3	985.1	1644.7	1648.1	1652.3
DMF- Water (30:70 %w/w)						
0.2003	979.6	972.5	970.7	1625.2	1629.1	1642.3
0.4000	980.5	977.6	973.2	1635.4	1639.5	1648.6
0.6005	982.1	980.0	977.8	1647.6	1651.7	1654.9
0.7999	985.5	984.5	980.1	1652.8	1657.9	1661.1
1.0000	990.2	988.7	985.3	1667.1	1669.2	1672.5

Table 2 Adiabatic compressibility (β), apparent molal compressibility (ϕ_k), and apparent molal volume (ϕ_v)

Molality of salt (<i>m</i>)	$\beta \times 10^{10} (\text{pa}^{-1})$			$-\phi_k \times 10^{10} (\text{m}^2.\text{N}^{-1})$			$-\phi_v (\text{m}^3.\text{mol}^{-1})$		
	Temperature (K)			Temperature (K)			Temperature (K)		
	303	308	313	303	308	313	303	308	313
TEAB									
DMF- Water (10:90 %w/w)									
0.0000	4.1808	4.1630	4.1748	-	-	-	-	-	-
0.2001	4.0959	4.0936	4.0833	499.09	432.14	427.56	17.87	20.47	40.75
0.4013	4.0634	4.0621	4.0569	352.23	309.93	411.99	14.25	15.03	28.29
0.6002	4.0256	4.0216	4.0132	309.17	298.16	370.54	13.58	14.03	24.24
0.8016	3.9962	3.9854	3.9829	288.65	274.27	316.94	12.07	13.61	20.46
1.0001	3.9490	3.9524	3.9488	278.30	267.34	304.88	11.46	12.63	18.87
DMF- Water (20:80 %w/w)									
0.0000	3.9665	3.9565	3.9532	-	-	-	-	-	-
0.2009	3.9456	3.9501	3.9443	389.05	364.25	364.48	21.41	28.16	30.40
0.4001	3.9210	3.9123	3.9040	274.14	275.37	283.86	14.67	16.59	26.12
0.6000	3.8714	3.8688	3.8583	256.79	258.08	237.02	14.58	14.23	20.69
0.8002	3.8395	3.8344	3.8228	234.96	243.52	222.57	11.63	13.59	17.98
1.0010	3.7913	3.7872	3.7798	218.90	230.17	213.97	11.03	13.53	16.54
DMF- Water (30:70 %w/w)									
0.0000	3.9142	3.8643	3.8558	-	-	-	-	-	-
0.2002	3.8110	3.8149	3.7987	372.10	287.77	453.84	22.10	26.23	32.62
0.4003	3.7919	3.7756	3.7549	366.97	277.94	377.46	18.17	18.72	26.93
0.5999	3.7444	3.7462	3.7287	354.30	266.95	319.58	16.83	17.24	21.59
0.8002	3.6913	3.6859	3.6750	344.58	258.72	306.73	15.67	16.99	20.71
1.0002	3.6722	3.6583	3.6395	302.03	254.99	294.51	15.32	15.85	18.02
TPAB									
DMF - Water (10:90 %w/w)									
0.2002	4.0518	4.0589	4.0471	621.66	656.42	683.40	32.40	42.77	58.81
0.4001	4.0190	4.0115	4.0032	508.08	484.24	581.93	24.79	25.36	36.65
0.6003	3.9757	3.9787	3.9655	431.43	396.20	471.49	21.47	21.52	29.42
0.8002	3.9398	3.9178	3.9023	384.01	386.03	449.93	19.81	19.98	26.20
1.0003	3.8966	3.8737	3.8571	360.64	369.85	416.75	18.30	19.37	23.74
DMF - Water (20:80 %w/w)									
0.2003	3.9214	3.9125	3.9030	583.52	353.73	453.04	33.88	39.92	51.20
0.4006	3.8649	3.8746	3.8628	425.84	325.94	335.94	24.31	25.15	39.22
0.6003	3.8429	3.8316	3.8246	379.74	312.41	315.86	18.61	20.89	22.08
0.8000	3.7827	3.7804	3.7750	303.79	294.68	290.42	17.94	19.66	20.50
1.0004	3.7247	3.7214	3.7183	289.21	283.33	286.89	17.52	17.26	19.55
DMF - Water (30:70 %w/w)									
0.2003	3.8745	3.8649	3.8195	527.33	358.21	361.78	28.29	29.16	35.74
0.4000	3.8133	3.8055	3.7807	452.06	310.30	343.22	25.50	21.92	24.38
0.6005	3.7509	3.7403	3.7343	449.17	300.90	322.20	20.19	19.86	24.19
0.7999	3.7145	3.6978	3.6955	384.78	277.00	309.96	19.73	19.50	21.14
1.0000	3.6337	3.6301	3.6283	359.54	264.56	289.85	19.19	18.73	19.30

4. CONCLUSION

The parameters discussed in this paper also recommending the ion-solvent interactions predominate over ion-ion interaction for TEAB/TPAB in different aqueous binary mixture of DMF at all experimental temperature which is discussed earlier.

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